PB-216 846

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1959

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INTRODUCTION

As a portion of a program of the study of individual species in collections from polluted atmospheres, it was felt desirable to develop a method for the separation and identification of aliphatic amines. Several alternative methods were considered,[4,5,6] but in view of experience in our laboratory[3] with the method of DeJonge[1,2] it was decided that an investigation should be made of the possible use of the benzamides as suitable derivatives for paper chromatography. As has been previously noted,[3] it is possible greatly to extend the lower limit of such a technique by the use of carbon-14 labelling.

PROCEDURE

Materials. Chemicals used, except where otherwise noted, were reagent grade, or the purest available. Benzoic acid, labelled with carbon-14 in the carboxyl group, was purchased from Tracer Laboratory. It had a nominal specific activity of 1.46 mc/mm. Benzoyl chloride was prepared from this in the usual way[9].

Lower molecular weight benzamides for calibration purposes were prepared by the Schotten-Bauman reaction[7]. The higher molecular weight derivatives were made by the method of Sasin, et al.[8].

Schleicher and Schuell papers 2040 a gl. and 2045 a gl. were used as indicated for the paper chromatographs. Radioautographs were prepared using Eastman Kodak x-ray film, no screen.

DeJonge's systems are as follows:

System M: 80% Methanol-cyclohexane
Ratio 20:80

System P: 50% Ethanol-cyclohexane
Ratio 20:80

System E: 20% Propanol-cyclohexane
Ratio 20:80

Determination of RF values. A solution of each pure benzamide containing approximately 2 mg/ml. was chromatographed according to the procedure of DeJonge[1] at 20°C. The spots were located in the usual fashion by means of ultraviolet light. The results are tabulated in Table I for DeJonge's system M and E. System P was also tried, but found unsatisfactory. Mixtures of benzamides containing approximately 2 milligrams per milliliter of each benzamide were found to separate adequately in most cases, as would be anticipated by RF values given.

Determination of lower limit of identification. For this purpose, very dilute solutions of the radiocarbon-type benzamides were chromatographed, placed on x-ray film for eight to ten days and the radioautographs developed in the usual way. The lower limit of identification was found to be approximately 2.5 micrograms of each benzamide. Quantitative measurements could be made on larger amounts by elution according to DeJonge and Verhage[2] and by a measurement of the absorbance at 225 mu with a Beckman spectrophotometer, Model DU.

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Preparation of air samples. Samples of airborne particulate matter collected on glass fiber filters were supplied by the National Air Sampling Network, U. S Public Health Service. A quantity of filter bearing 3 to 8 grams of particulate matter was chopped into small squares, dampened with sodium hydroxide, and extracted with three 250 ml. portions of anhydrous redistilled ether by shaking. Since it was found that all of the amines were removed from a mixture of amine salts in two ether extractions of 20 minutes each, by reacting the extract with benzoyl chloride, it was assumed that a total extraction time of 11-12 hours with ether and sodium hydroxide was sufficient to remove any amines from the particulate matter. After this interval the extract was decanted through a filter and acidified with hydrogen chloride gas. The volume of extract was reduced to approximately 50 ml. by means of an air stream. A slight excess of 10% sodium hydroxide was added, and 0.1 to 0.15 ml. of radioactive benzoyl chloride was added, and the reaction mixture was shaken for 20 minutes. The benzamides were extracted with three portions of benzene, to make a total volume of approximately 40 ml. The benzene solution was evaporated in an air stream to a volume of 2-3 ml., diluted to 5 ml. with additional benzene, and chromatographed as described above.

Atmospheric vapors were collected in approximately 10% sulfuric acid by means of a Smith-Greenburg impinger. The collected sample was neutralized with sodium hydroxide in a closed flask with a sidearm dipping into a container of ether. This trapped any vapor liberated during the neutralization. The aqueous layer was then extracted with ether, the ether layers were combined, and were treated as indicated above for the particulate matter.

RESULTS AND DISCUSSION

The data in Table I gives a survey of mean RF values of the benzamides. These values are not to be taken as absolute, since they are influenced by some of the usual factors which cause variation in RF values. The presence of foreign material as are found in air samples tend to depress the values still more.

Homologous benzamides are separated satisfactorily on Schleicher and Schuell 2040 a gl. paper with a development time of three hours, while isomeric benzamides, with the exception of the pair N-propyl and N-isopropyl, are not completely separated. Although the pair N-decyl and N-dodecyl benzamides are incompletely separated on S. & S. 2040 a gl. paper in the standard development time, these are very satisfactorily separated on S. & S. 2045 a gl. paper.

While secondary benzamides are separated from each other, they are not completely separated from some of the primary benzamides, so that spectra must be relied upon to differentiate them[10].

A typical separation of a mixture of N-ethyl, N-sec.-butyl, N-hexyl, N-octyl, and N-decyl benzamides is illustrated in Figure 1, with the quantities increasing from 15 to 50 µg, while in Figure 2 is illustrated a separation of N-methyl, N-propyl, N-isoamyl, and N-heptyl benzamides of the same magnitude.

A radioautograph of an air particulate sample from Los Angeles, California showed two distinct spots at RF values corresponding to N-ethyl and possibly N-propyl plus benzoic acid. By rechromatographing these areas in system E they have been shown to be N-ethyl benzamide, and benzoic acid formed by the hydrolysis of benzoyl chloride. A larger area near the front of the chromatogram was produced by a yellowish material which gave a reddish fluorescence under ultraviolet light.

A similar radioautograph of air particulate matter from Birmingham, Alabama, showed no such spots other than benzoic acid and the large frontal smear.

Figure 3 is a representation of a chromatogram of a sample of atmospheric vapors collected in approximately 10% H_2SO_4 in a New York City fish market. Two distinct spots are visible at RF values corresponding to N-methyl benzamide and the expected benzoic acid area. The approximate values of the benzamides found in both the Los Angeles and the New York sample can be seen in Table II. These have been estimated by a modification of the isotope dilution method[11] and by spectrophotometry.

ACKNOWLEDGMENTS

The authors are indebted to Dr. L. M. Marshall for suggesting the problem and for stimulating discussions on the subject. We are also grateful to Dr. Morris B. Jacobs for furnishing us with the sample from New York City. The Los Angeles sample was collected by the National Air Sampling Network.

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FIGURES

Figure 1. Radioautograph illustrating separation of even straight chain mixtures of N-benzamides.

Figure 2. Radioautograph of odd mixtures of straight chain N-benzamides.

Figure 3. Radioautograph of atmospheric vapors, New York City.

TABLE I

N-BENZAMIDES

RF VAL. x 100

N-Benzamide	System M	System E
S & S 2040 a gl. paper		
N-methyl	3.60	4.49
N-ethyl	8.35	16.68
N-propyl	16.11	30.59
N-isopropyl	22.13	41.50
N-sec-butyl	33.75	58.29
N-isobutyl	29.63	61.87
N-n-butyl	33.90	
N-isoamyl	42.82	68.96
N-hexyl	62.62	82.28
N-heptyl	71.19	
N-octyl	81.82	
N-decyl	87.03	
N-dodecyl	89.30	
2-ethyl-N-hexyl	80.83	95.68
1,3-dimethyl-N-butyl	65.31	81.89
benzoic acid	16.0-19.43	44.18
N,N-diisopropyl	84.13	
N,N-diisobutyl	92.69	
S & S 2045 a gl. paper		
N-decyl	75.37	
N-dodecyl	82.02	

TABLE II

N-BENZAMIDES FOUND IN AIR SAMPLES

Sample	Benzamide Found	Mg. Benzamide	Amine Mg.	Total Air Flow m^3	Amine mg/m^3 air
Los Angeles	N-ethyl	3.045	0.920	1,800	5.1×10^{-5} (1)
Birmingham	None(2)	less than identifiable quantity		25,167	------
New York	N-methyl	3.516	0.808	5.44	0.149

(1) The air flow is estimated as an average of 2000 m^3 per 24 hours in the absence of specific air flow data.

(2) No individual benzamide could be identified.